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SUMMARY

A modified expression for the Gibbs free energy of formation of ion-induced microclusters in binary vapor mixtures has previously been developed by including the effects of microscopic surface tension, field-dependent, nonlinear, dielectric behavior of liquids, and neutral clustering prior to ion-induced nucleation. It has been further simplified by using an empirical correction factor for the electrostatic term instead of the tedious, time-consuming computations required previously. The electrostatic correction factor has been obtained by comparing the simplified-theory calculations for free energy of selected ion-hydrate formation with more rigorous molecular-dynamics calculations. The simplified Gibbs free-energy expression has been applied to calculate the spectral distribution of ion-H_2O-H_2SO_4 microclusters for various combinations of relative humidity and relative acidity. Because of the higher contribution of the electrostatic energy term in the simplified expression, the predicted microcluster spectra are broader and contain more of the larger ion clusters than predicted by the earlier theories. These trends are consistent with recently reported experimental data on ion-induced binary nucleation.

INTRODUCTION

It is well-known that ions are present throughout the atmosphere. In the upper atmosphere, galactic cosmic rays, solar flares, and ultraviolet radiation from the Sun induce ionization of gaseous molecules. Closer to the surface of the Earth, radioactivity associated with uranium/thorium series ores as well as coal combustion products help to produce primary ions. The ions act as foreign centers and greatly enhance the nucleation process. They facilitate the formation of stable, ultrafine, prenucleation clusters, especially in the presence of traces of pollutant gases. Rocket measurements show that stable ion clusters are part of the aerosol size spectrum in the stratosphere. (See refs. 1 and 2.) Ion-induced gas-to-particle conversion plays an important role in the formation of ultrafine aerosols emitted from high-temperature combustion sources. (See ref. 3.) Thus, a study of the mechanism of ion-induced nucleation is very important in gaining a better understanding of space and Earth environments. In the present study, we address the problem of nucleation processes induced by the presence of ions in a binary mixture of vapors. An empirical modification of the classical nucleation theory is presented, and the cluster spectra obtained using this modified approach are compared with other existing theories.

The conventional Thomson theory (ref. 4) for hydration of ions is developed from the ion-liquid drop theory and hence suffers from all the shortcomings of the liquid drop model. (See refs. 5 through 10.) According to this theory, the free energy of formation of ion clusters is composed of three parts: (1) Volume energy, (2) surface energy, and (3) electrostatic energy. There are two major criticisms of the classical ion-liquid droplet theory. First, bulk values are used in the volume and surface-energy terms, even for small clusters. Second, the electrostatic-energy term is treated by considering the ion as embedded in a uniform dielectric medium and thus neglecting the strong intermolecular interaction between the ion core and its surrounding molecules. To improve the conventional theory, Chan and Mohnen (ref. 9) developed a semimolecular ion-nucleation theory which includes corrections for the aforementioned defects. Briant and Burton (ref. 11) adopted a molecular approach

that is partially based on molecular dynamics. Some of the corrections proposed in reference 9 have been extended further so that the theory can apply to ion-induced nucleation in binary mixtures of vapors. (See ref. 12.)

It is the purpose of this paper to show that use of the microscopic surface tension and appropriate scaling of the electrostatic-energy term in the Thomson theory for ion hydrates can produce good agreement with results obtained with the more rigorous Chan and Mohnen (ref. 9) and Briant and Burton (ref. 11) models. The simple scaling corrections thus obtained are then extended to the ion-induced nucleation in binary mixtures of vapors. Predicted results for the formation of ion-H_2O-H_2SO_4 clusters based on the Thomson theory for binary mixtures of vapors (model I), the more complicated modified theory (ref. 12) for ion-induced binary nucleation (model II), and the present modified Thomson theory (model III), are compared, and the implications are discussed in the following sections.

SYMBOLS

E	electric field, $\frac{Q}{\varepsilon(r)r^2}$
ΔG	free energy of droplet formation
ΔG_B	bulk energy term
ΔG_E	electrostatic energy term
ΔG_o	free-energy change without effect of formation of sulfuric acid hydrate
ΔG_S	surface energy term
g	field-dependent Kirkwood factor
k	Boltzmann constant
$N_{A,B}$	total number of molecules of component A or B in system
$n_{A,B}$	number of molecules of component A (water) or B (sulfuric acid) in cluster
$P(n_A,n_B)$	probability of occurrence for the ion cluster containing n_A molecules of component A and n_B molecules of component B
$p_{A,B}$	equilibrium vapor pressure of component A or B
p_A^o	saturation vapor pressure of component A
p_B^o	saturation vapor pressure of component B
$p_{A,B}^{sol}$	equilibrium vapor pressure of component A or B over flat surface of solution
$p'_{A,B}$	partial pressure of component A or B after sulfuric acid hydrate formation
Q	ionic charge on cluster

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Q_{eff} effective ionic charge on cluster

r radius of droplet

r_1 ionic radius

S saturation ratio

S_A relative humidity (R.H. in tables)

S_B relative acidity (R.A. in tables)

T absolute temperature

α empirically adjustable scaling parameter

α_A water activity

α_B acid activity

β $= \frac{3}{2kT}\left(\frac{\eta^2 + 2}{3}\right)\mu_o g^{1/2}$

γ charge scaling factor

δ Tolman coefficient

ε dielectric constant of mixture

ε_o bulk dielectric constant of mixture

$\varepsilon(r)$ radius-dependent dielectric constant

η internal refractive index of liquid

μ_o dipole moment in absence of field

σ surface tension

σ_o plane surface tension

THEORETICAL CONSIDERATIONS

The classical Thomson theory states that the free energy of formation ΔG for an ion-hydrate cluster is given by

$$\Delta G = \Delta G_B + \Delta G_S + \Delta G_E \quad (1)$$

The bulk-energy term is given by

$$\Delta G_B = -n_A kT \ln S \quad (2)$$

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the surface-energy term is

$$\Delta G_S = 4\pi r^2 \sigma \tag{3}$$

and the electrostatic term is

$$\Delta G_E = \frac{Q^2}{2}\left(1 - \frac{1}{\epsilon}\right)\left(\frac{1}{r} - \frac{1}{r_1}\right) \tag{4}$$

where

n_A number of molecules of component A

k Boltzmann constant

T absolute temperature

S saturation ratio (ratio of partial pressure to saturation pressure)

r radius of ion cluster

σ surface tension

Q ionic charge

ϵ dielectric constant

r_1 ionic radius

In the calculation of the surface-energy term (eq. (3)), the bulk surface-tension value is used, and in equation (4), the ion is assumed to be embedded in a uniform dielectric medium. Results obtained using the Thomson theory do not agree with the semimolecular theory developed by Chan and Mohnen (ref. 9) as well as with the molecular theory, based partially on molecular dynamics, developed by Briant and Burton (ref. 11). A major source of error is the use of the macroscopic surface tension and the neglect of the strong intermolecular interactions between the ion core and the surrounding water molecules. It is well recognized that the surface tension is curvature-dependent. (See ref. 13.) The influence of this curvature effect on the free energy of formation of microclusters has been discussed in several recent papers. (See refs. 13 and 14, for example.) The Tolman correction for the surface tension (ref. 13) is simple and widely used. Using the Tolman coefficient δ, we have

$$\sigma(r) = \sigma_o\left(1 + \frac{2\delta}{r}\right)^{-1} \tag{5}$$

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where $\sigma(r)$ is the surface tension of a microcluster of radius r and σ_o is the plane surface tension. Vogelsberger (ref. 15) suggested 0.92 Å as the value of δ for water.

The correction for the electrostatic term is more complicated. It takes into account the influence of the intermolecular interaction between the ion core and the surrounding molecules as well as the breakdown of the linear correlation between dielectric polarization and electric-field strength. Corrections for this defect are discussed by Chan and Mohnen (ref. 9). Briant and Burton (ref. 11) treat this problem by applying molecular-dynamics calculations. Since the computations for the free energy of formation of gas-phase ion hydrates by Chan and Mohnen (ref. 9) and Briant and Burton (ref. 11) are among the most accurate, one simple approach to correct for this defect is to empirically scale the electrostatic term so that good agreement is reached between the present calculations and those of references 9 and 11. Incorporating the Tolman correction for the surface tension and the empirical scaling factor for the electrostatic term, the modified expression for the Gibbs free energy is

$$\Delta G = -n_A kT \ln S + 4\pi r^2 \sigma_o \left(1 + \frac{2\delta}{r}\right)^{-1} + \gamma\left(\frac{Q^2}{2}\right)\left(1 - \frac{1}{\varepsilon}\right)\left(\frac{1}{r} - \frac{1}{r_1}\right) \tag{6}$$

where γ is the charge scaling factor. The value of ΔG is critically dependent on the value of γ.

Free energies of F^- and Cs^+ hydrates have been calculated using equation (6). The initial hydrate growth is largely determined by the electrostatic interaction between the ion and the surrounding molecules and is, therefore, strongly dependent on the value of γ. A small change ($\approx$10 percent) in the value of γ can produce a measurable change in the ion-hydrate spectrum. Figures 1 and 2 show the comparison between various theories for the calculation of ΔG for two ion hydrates. The agreement is especially good between the calculations of Briant and Burton and those of the present model for $\gamma = 1.3$. The scaling procedure suggests that when microscopic surface tension is taken into account, the effect of the interaction between the ion core and the surrounding molecules can be approximated by using an effective charge distribution of

$$Q_{eff} = \sqrt{1.3Q} = 1.14Q \tag{7}$$

A value of Q_{eff} greater than Q implies relatively greater importance of the electrostatic term than of the free-energy change of the neutral portion of the cluster in the prenucleation stages.

Suck (ref. 16) has also calculated the contribution of the electrostatic interaction energy between the ion and the surrounding molecules in the cluster. In the

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limiting case of zero polarizability and zero dipole moment associated with an ion, his expression for the electrostatic term reduces to the following form:

$$\Delta G_{\text{electrostatic}} = \frac{9}{2}\left[\frac{\varepsilon(\varepsilon - 1)}{(2\varepsilon + 1)(\varepsilon + 2)}\right]\alpha Q^2\left(\frac{1}{r} - \frac{1}{r_1}\right)$$

$$\approx \frac{9\alpha}{2}\left(\frac{Q^2}{2}\right)\left(1 - \frac{1}{\varepsilon}\right)\left(\frac{1}{r} - \frac{1}{r_1}\right) \tag{8a}$$

where α is an empirically adjustable scaling parameter. Using equation (8a), Suck calculated free energy of formation of $F^-\cdot(H_2O)_n$ and $Cs^+\cdot(H_2O)_n$ clusters for direct comparison with computations of Briant and Burton (ref. 11). He found good agreement for $\alpha = 1/3$, thus giving

$$Q_{\text{eff}} = \sqrt{1.5}Q = 1.22Q \tag{8b}$$

However, Suck's primary interest was to assess the importance of the electrostatic term to the total free-energy change owing to the presence of ions during the cluster formation. This was in contrast to the conventional Thomson theory, in which the electrostatic term is usually added to the free-energy change of a neutral drop to obtain the total free-energy change. Consequently, Suck had made no changes in the volume and the surface-energy terms (i.e., he did not include size dependence of the surface tension in his calculations).

Figures 1 and 2 show that the same value of the scaling factor (i.e., $\gamma = 1.3$) applies equally well for the positive and negative ions and works fine for clusters containing up to 30 water molecules. The concept of the scaling factor for the electrostatic-energy term is further extended to the ion-induced nucleation in a binary mixture of vapors in the following section.

COMPARISON OF DIFFERENT BINARY ION-NUCLEATION THEORIES FOR MIXTURE OF WATER AND SULFURIC ACID VAPORS

When the Thomson theory is extended to binary ion nucleation for a mixture of vapors (ref. 17), it states that the free energy required to form a droplet ΔG with n_A molecules of substance A and n_B molecules of substance B around an ion core with charge Q and radius r_1 (model I) is given by the following equation:

$$\Delta G(n_A, n_B) = -n_A kT \ln\frac{S_A}{\alpha_A} - n_B kT \ln\frac{S_B}{\alpha_B} + 4\pi r^2\sigma_o + \frac{Q^2}{2}\left(1 - \frac{1}{\varepsilon_o}\right)\left(\frac{1}{r} - \frac{1}{r_1}\right) \tag{9}$$

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where

$$S_A = \frac{p_A}{p_A^o} \tag{10a}$$

$$\alpha_A = \frac{p_A^{sol}}{p_A^o} \tag{10b}$$

$$S_B = \frac{p_B}{p_B^o} \tag{10c}$$

$$\alpha_B = \frac{p_B^{sol}}{p_B^o} \tag{10d}$$

where

p_i equilibrium vapor pressure of specie i

p_i^o saturation vapor pressure of pure specie i

p_i^{sol} equilibrium vapor pressure of specie i over flat surface of solution

In this paper, n_A and n_B are used to denote the number of water and sulfuric acid molecules in the ion cluster, respectively.

A more complex equation for calculation of the free energy of droplet formation in binary mixtures has been developed by Singh et al. (See ref. 9.) The free energy of formation of the ion clusters (model II) takes the form

$$\Delta G(n_A,n_B) = -n_A kT \ln \frac{S_A}{\alpha_A} - n_B kT \ln \frac{S_B}{\alpha_B} + 4\pi r^2 \sigma_o \left(1 + \frac{2\delta}{r}\right)^{-1}$$

$$- n_B kT \ln \frac{p_B'}{p_B} + \frac{Q^2}{2}\left(\frac{1}{r} - \frac{1}{r_1}\right) + \frac{Q^2}{2}\int_{r_1}^{r} \frac{1}{\varepsilon(r) r^2}\, dr \tag{11}$$

where δ is the Tolman coefficient, p_B' is the actual vapor pressure of the sulfuric acid taking into account the presence of the sulfuric acid hydrates, and $\varepsilon(r)$

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is the radius-dependent dielectric constant. The first two terms on the right-hand side of equation (11) are the bulk energy terms. The third term represents the surface energy, taking into account the effect of curvature of small droplets. The fourth term accounts for the effect of the formation of neutral sulfuric acid hydrates. The value of p_B'/p_B in this term is obtained by solving the following equation numerically (refs. 12 and 18):

$$\sum_{n_A}\sum_{n_B} N_A\left(\frac{p_B'}{p_B}\right)^{n_B}\exp\left[-\frac{\Delta G_o(n_A,n_B)}{kT}\right] = N_B\left(1-\frac{p_B'}{p_B}\right) \tag{12}$$

where N_A and N_B are the total number of molecules for A and B in the system and ΔG_o is the free-energy change without the effect of the formation of sulfuric acid hydrate. The fifth and sixth terms in equation (11) describe the electrostatic-energy contribution. The value of $\varepsilon(r)$ can be obtained by solving the following equations (refs. 12 and 19):

$$\varepsilon(r) = \eta^2 + \left(\varepsilon_o - \eta^2\right)\frac{3}{\beta E}\left(\frac{1}{\tanh(\beta E)} - \frac{1}{\beta E}\right) \tag{13a}$$

where

$$E = \frac{Q}{\varepsilon(r)r^2} \tag{13b}$$

$$\beta = \frac{3}{2kT}\left(\frac{\eta^2+2}{3}\right)\mu_o g^{1/2} \tag{13c}$$

Here, η is the internal refractive index of the liquid, μ_o is the dipole moment in the absence of the field, and g is the field-dependent Kirkwood factor (ref. 20) defined as follows:

$$g = g_0 + g_1E^2 + g_2E^4 + g_3E^6 + \ldots \tag{13d}$$

If higher terms in E are neglected, then

$$g \approx 1 + \frac{g_0 - 1}{1 - \left[g_1E^2/(g_0 - 1)\right]} \tag{13e}$$

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The values of g_0 and g_1 for water* given by Liszi et al. (ref. 19) are as follows: $g_0 = 2.8$ and $g_1 = -0.56 \times 10^{-8}$ (when E is expressed in esu).

Using a simplified approach to calculate the electrostatic-energy term, equation (11) can be modified as follows (model III):

$$\Delta G = -n_A kT \ln \frac{S_A}{\alpha_A} - n_B kT \ln \frac{S_B}{\alpha_B} + 4\pi r^2 \sigma_o \left(1 + \frac{2\delta}{r}\right)^{-1}$$

$$+ \gamma\left(\frac{Q^2}{2}\right)\left(1 - \frac{1}{\varepsilon}\right)\left(\frac{1}{r} - \frac{1}{r_1}\right) - n_B kT \ln \frac{p'_B}{p_B} \qquad (14)$$

where $\gamma = 1.3$.**

The value of surface tension σ and the variation of p_A^{sol} and p_B^{sol} with composition are available in the literature. (See refs. 21 and 22.)

A major advantage of model III over model II is that by empirically adjusting the electrostatic term, the complicated computations involved in model II are avoided. In the limiting case, if $n_B = 0$ in model III, the free-energy change given by equation (14) is the same as that given by equation (6), which has been shown to agree well with other more rigorous calculations, especially those of Briant and Burton (ref. 11). Computed cluster spectra for the three models under various relative-acidity and relative-humidity combinations are given in tables 1 through 3.

Figure 3 shows the spectra of calculated ion-H_2O-H_2SO_4 clusters for the three models (Relative humidity = 0.1 and Relative acidity = 1×10^{-5}). The value of the $H^+ \cdot H_2O$ ion radius in these calculations is assumed to be 1.38 Å. For model I, the ion clusters are mainly confined to groups containing one or two sulfuric acid molecules with a relatively small number of water molecules attached to the ion core. For model II, the ion-cluster spectrum is spread out, and ion clusters containing higher numbers of sulfuric acid and water molecules are more common. For model III, there is an appreciable amount of the group containing three sulfuric acid molecules accompanied by further spectral broadening. The peak intensity (relative abundance) of the cluster distribution is lowered while the spectrum gets broader. Table 4 shows that the mean radius of the ion clusters increases from model I to model II to model III. Hence, the effect of the modifications included in model II over the conventional extended Thomson theory (model I) is to broaden the ion-cluster spectrum, producing a more even distribution and bigger ion clusters. This results in a larger mean radius in accord with the experimental results reported by Singh et al. (See ref. 23.) These features are further strengthened in model III.

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*For dilute clusters, the g factors are approximately the same as for water.

**The optimum value of γ for ion-H_2O clusters is 1.3. The same value of γ has been assumed for ion-H_2O-H_2SO_4 clusters.

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CONCLUDING REMARKS

Examination of the three models reveals that the microscopic surface tension used in models II and III greatly reduces the surface-energy contribution for small ion clusters and hence enhances the formation of ultrafine ion clusters. Comparison of models I, II, and III also shows that the electrostatic-energy term is important. A slight increase in the effective charge of the ion facilitates the formation of larger and more stable prenucleation clusters. The effect of the neutral sulfuric acid hydrates is small, especially when the relative humidity is low.

From the comparison of various models for various combinations of relative humidity and relative acidity, it can be seen that the Thomson theory (model I) consistently predicts smaller clusters with narrowly peaked distributions, whereas the modified theories (models II and III) predict larger clusters with broader distributions. These latter trends are consistent with recently reported experimental results.

The modifications involving the curvature dependence of the microscopic surface tension and strong intermolecular interaction between the ion core and its surrounding molecules introduce large differences between the predicted spectral distributions of the ion-H_2O-H_2SO_4 clusters for the various models. Because of the higher contribution of the electrostatic-energy term in the present model (model III), the predicted microcluster spectrum becomes even broader, and more of the larger ion clusters are included. The validity of the charge scaling-factor model has yet to be tested. However, the agreement in the values of free energy of formation of F^- and Cs^+ hydrates in the present model with other, more rigorous, theories suggests that it may be a reasonably accurate model to use for free-energy calculations in the region of very small clusters.

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TABLE 1.- COMPARISON OF PREDICTED ION-CLUSTER DISTRIBUTIONS FOR VARIOUS MODELS

WITH R.A. = 1×10^{-6} AND R.H. = 0.1

[Only ion-cluster intensities greater than 1 percent in the spectrum are listed]

Model	$P(n_B,n_A)$ for n_B,n_A values of -										$\sum_{n_A} P(n_B,n_A)$
	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	1,10	1,11	(1,x)
I		2.5%	19.7%	33.7%	22.3%	8.1%	1.8%				88.1%
II			5.0%	17.1%	20.7%	12.6%	4.5%	1.1%			61.0%
III					2.9%	4.3%	3.3%	1.6%			12.1%
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	(2,x)
I				2.9%	4.1%	2.4%					9.4%
II				4.4%	11.2%	11.3%	6.9%	2.8%			36.6%
III				2.3%	11.6%	21.7%	22.8%	14.9%	6.0%	2.1%	81.4%

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TABLE 2.- COMPARISON OF PREDICTED ION-CLUSTER DISTRIBUTIONS FOR VARIOUS MODELS

WITH R.A. = 1×10^{-4} AND R.H. = 0.1

[Only ion-cluster intensities greater than 1 percent in the spectrum are listed]

Model	$P(n_B,n_A)$ for n_B,n_A values of -													$\sum_{n_A} P(n_B,n_A)$
	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9	1,10	1,11	1,12	1,13	1,14	(1,x)
I II III			1.4%	2.3%	1.6%									5.3%
	2,2	2,3	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	2,12	2,13	2,14	(2,x)
I II III			6.6%	20.2% 6.0%	28.2% 15.3% 1.7%	16.6% 15.6% 3.2%	6.1% 9.5% 3.4%	1.5% 3.8% 2.2%						79.2% 50.2% 10.5%
	3,2	3,3	3,4	3,5	3,6	3,7	3,8	3,9	3,10	3,11	3,12	3,13	3,14	(3,x)
I II III					2.6% 3.2% 1.5%	3.7% 7.7% 5.6%	3.1% 10.9% 11.8%	1.9% 10.7% 16.8%	5.2% 11.8%	2.2% 6.9%	2.4%			11.3% 39.9% 56.8%
	4,2	4,3	4,4	4,5	4,6	4,7	4,8	4,9	4,10	4,11	4,12	4,13	4,14	(4,x)
I II III							1.5%	3.5%	5.5%	6.6%	4.8%	2.3%	1.1%	25.3%

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TABLE 3.- COMPARISON OF PREDICTED ION-CLUSTER DISTRIBUTIONS FOR VARIOUS MODELS

WITH R.A. = 1×10^{-6} AND R.H. = 0.5

[Only ion-cluster intensities greater than 1 percent in the spectrum are listed]

Model	$P(n_B,n_A)$ for n_B,n_A values of -																	$\sum_{n_A} P(n_B,n_A)$
	1,4	1,5	1,6	1,7	1,8	1,9	1,10	1,11	1,12	1,13	1,14	1,15	1,16	1,17	1,18	1,19	1,20	(1,x)
I		2.1%	6.9%	12.6%	13.9%	10.8%	6.9%	3.5%	1.6%									58.3%
II				1.6%	2.8%	3.5%	3.3%	2.5%	1.6%									15.3%
III																		
	2,4	2,5	2,6	2,7	2,8	2,9	2,10	2,11	2,12	2,13	2,14	2,15	2,16	2,17	2,18	2,19	2,20	(2,x)
I			1.3%	3.7%	6.8%	8.5%	7.1%	5.6%	3.3%	1.8%								38.1%
II				1.4%	4.4%	8.8%	11.1%	13.1%	10.9%	8.6%	5.1%	2.9%	1.5%					67.8%
III					2.2%	4.4%	7.6%	9.4%	10.5%	8.6%	6.7%	4.5%	2.6%	1.4%				57.9%
	3,4	3,5	3,6	3,7	3,8	3,9	3,10	3,11	3,12	3,13	3,14	3,15	3,16	3,17	3,18	3,19	3,20	(3,x)
I								1.3%	1.7%	2.2%	2.0%	1.7%	1.3%					10.2%
II								1.2%	2.1%	3.7%	4.4%	4.8%	4.8%	3.8%	2.8%	2.0%	1.1%	30.7%
III																		

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TABLE 4.- MEAN RADII OF ION-CLUSTER SPECTRA FOR VARIOUS MODELS

WITH R.H. = 0.1

$$\left[\text{Mean radius} = \bar{r} = \frac{\sum_i P_i r_i}{\sum_i P_i} \text{ when } P_i \text{ is the probability for radius } r_i\right]$$

Model	Mean radius for R.A. values of -				
	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}
I	3.67 Å	3.90 Å	4.15 Å	4.51 Å	5.77 Å
II	3.92 Å	4.18 Å	4.45 Å	5.04 Å	7.25 Å
III	4.29 Å	4.47 Å	4.83 Å	5.50 Å	7.35 Å

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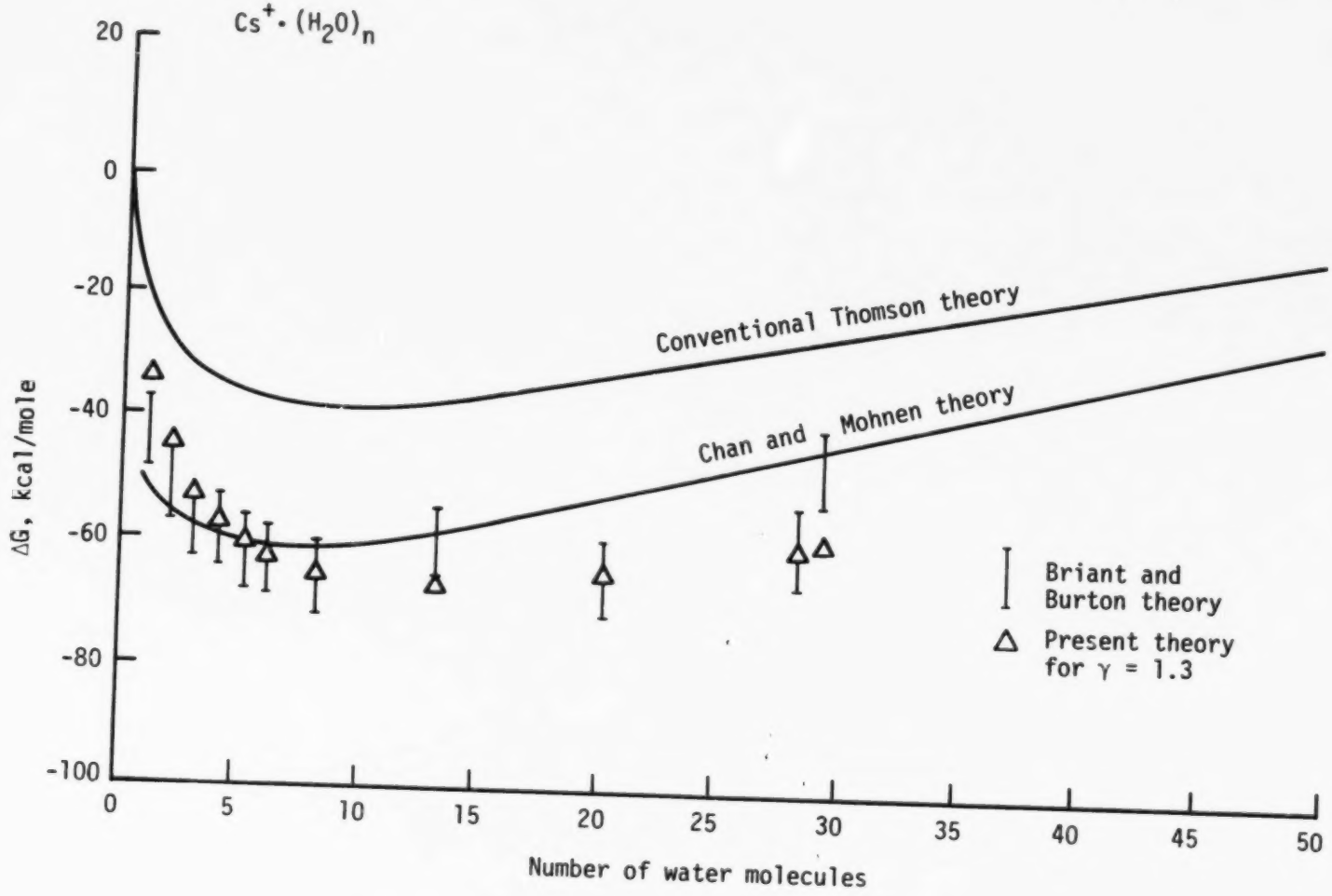

Figure 1.- Comparison of ΔG for four different models at $S = 1$ for $Cs^+ \cdot (H_2O)_n$ clusters.

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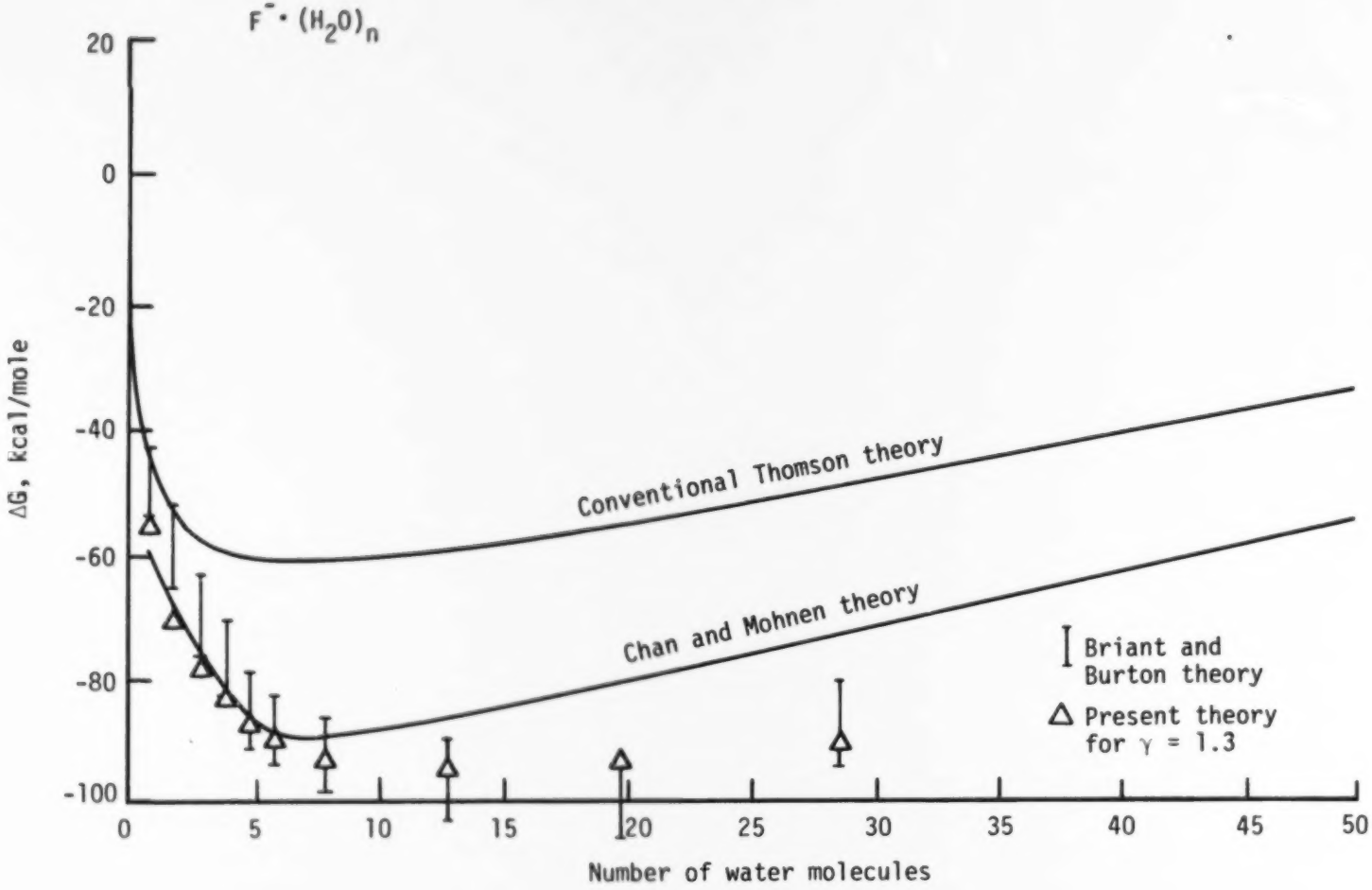

Figure 2.- Comparison of ΔG for four different models at $S = 1$ for $F^-\cdot(H_2O)_n$ clusters.

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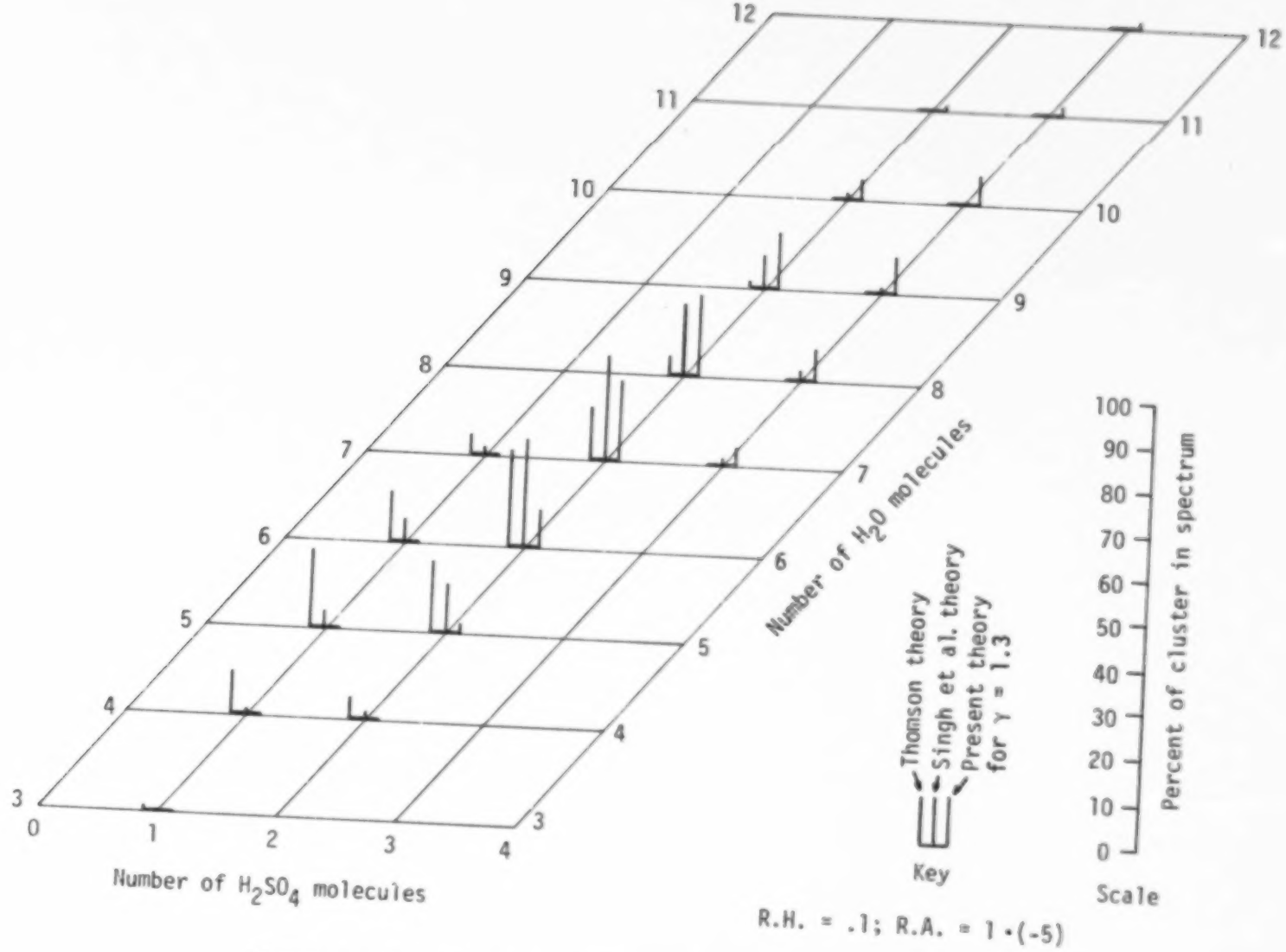

Figure 3.- Comparison of ion-H_2O-H_2SO_4 spectral distribution for three different models.

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15. Supplementary Notes

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16. Abstract

The Gibbs free energy of formation of ion-induced microclusters in binary vapor mixtures has been calculated using a simplified expression based on a modified microscopic surface tension and an empirical electrostatic correction factor. The electrostatic correction factor has been obtained by comparing the simplified theory calculations for free energy of selected ion-hydrate formation with the more rigorous molecular-dynamics calculations. Comparison between the cluster spectra predicted by the conventional Thomson theory, a more complex binary nucleation theory developed previously by the present authors, and the present model indicates that the magnitude of the electrostatic term is critical to the cluster-size spectrum. The present model predicts a broader spectrum, with a larger mean cluster size, than the other models.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
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